Electronic Supplementary Information

Contribution of lone-pairs to birefringence affected by Pb(II) coordination environment: A DFT investigation

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Numerical calculations details

After the electronic structures obtained, the imaginary part of the dielectric constant $\varepsilon_2(\omega)$ can be obtained by

$$\varepsilon_2 = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c} \left| < \varphi_k^c \middle| u \cdot r \middle| \varphi_k^v > \right|^2 \delta(E_k^c - E_k^v - E) \quad (1)$$

In which Ω is the volume of the elemental cell, *v*, and *c* represent the valence and conduction bands, respectively, and *u* is the vector defining the polarization of the electric field of the incident light. Since the dielectric constant describes a causal response, the real and imaginary parts are linked by a Kramers-Kronig transform. This transform is used to obtain the real part of the dielectric function, $\varepsilon_1(\omega)$, and then the refractive index *n*. In this paper, in order to get reliable refractive indices and birefringence, the number of conduction bands was set as three times that of valence bands.

During the calculation, under the norm-conserving pseudopotential (NCP), for Pb_2BO_3F, $Pb_2B_5O_9Cl$, PbB_4O_7 and $PbBa_2(B_3O_6)_2$, the following orbital electrons were treated as valence electrons: Pb:$5d^{10}6s^26p^2$, Ba:$5s^25p^66s^2$, B:$2s^22p^1$, O:$2s^22p^4$, F:$2s^22p^5$, Cl:$3s^23p^5$.